

INVESTIGATION OF THE POROUS STRUCTURE OF COAL USING ^{129}Xe NMR WITH SELECTIVE PRESATURATION AND SATURATION TRANSFER.

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ABSTRACT

The technique of selective low power presaturation applied to ^{129}Xe NMR of xenon adsorbed in coal can clearly demonstrate the existence of a distribution of similar adsorption sites for xenon, where the signals from xenon in these sites are not resolved as individual signals. Differences in inter/extra particle exchange in two coals of different rank, available from a saturation transfer technique, are significant. This technique can be used to investigate pore connectivity in microporous materials of unknown pore structure.

INTRODUCTION

Coal Microporosity. Coal microporosity accounts for most of its surface area. The largely amorphous physical structure of many coals, and the small dimensions of micropores (<20 Å), have made accurate assessment of the dimensions, size distribution, and connectivity of microporous networks in coal very difficult. Techniques such as SAXS (Bale et al., 1984; Lin et al., 1978; Larsen et al., 1995), X-ray diffraction (Hirsch, 1954), TEM (Lin et al., 1978; Harris and Yust 1976; 1981), gas adsorption (reviewed by Walker, 1981; Larsen et al., 1995), and others have all contributed to our understanding of coal porosity but, when applied to the characterization of microporosity, continue to have severe limitations.

There is wide acceptance of the following general model, however: "coals contain an interconnected pore network of high surface area, the slit-shaped pores having constricted openings of molecular dimensions...[and] coals contain both open and closed porosity." (Mahajan, 1991). The question of the extent of open or closed porosity is an area of continuing controversy, the major source of which is the large difference in coal surface area determined by adsorption of gases of similar molecular dimensions, or the molecular sieving effect. There are several critical reviews on the subject (Marsh, 1987; Mahajan, 1991; Walker and Mahajan, 1993). Molecular sieving effects are open to conflicting interpretations in terms of the pore structure of coal. Larsen et al. (1995) contend that the magnitude of the molecular sieving effect, along with the high fractal dimensionality of coal as determined by SAXS, are inconsistent with an interconnected, bottlenecked micropore network model; and that microporosity in coal exists primarily as isolated 'bubbles' in the solid matrix. This is a controversial conclusion; Larsen's results do not eliminate activated diffusion, as opposed to closed porosity, as a cause of molecular sieving according to Walker and Mahajan (1993). This issue is likely to remain unresolved without additional information that does not depend on gas uptake measurements.

Our approach to characterizing coal microporosity uses ^{129}Xe NMR spectroscopy (reviewed by Dybowski et al., 1991). ^{129}Xe NMR offers a way to derive different and more extensive information about xenon gas in its adsorbed state than would be available from classical adsorption experiments. The ^{129}Xe NMR signal contains information about both adsorption-site environment and dynamics of adsorbed xenon. In order to clarify the terminology used in this paper, we will note here that differences in adsorption sites in coal that affect the ^{129}Xe NMR signal chemical shift are size differences among micropores and possibly mesopores. However, given the heterogeneity of coal, it is possible that variations in pore wall chemistry may also affect the chemical shift. We will use the term adsorption site, meaning porosity of different size and/or chemistry, where appropriate. The results presented in this study can be used to address the question of whether the broad NMR signal from xenon adsorbed in coal arises from a distribution of similar adsorption sites and will demonstrate the differences in intra/extra particle exchange in two different pore networks, which can be interpreted in terms of whether the pores are open or closed, and how porosity changes with coal rank.

Theoretical basis of the NMR experiment. ^{129}Xe NMR spectra in this study detect xenon gas adsorbed on or in contact with the solid surface of coal. ^{129}Xe NMR has been previously applied to coal as a possible tool to determine micropore sizes (Wernett et al., 1990; Tsiao and Botto, 1992). The basic NMR concepts employed in this study are selective saturation and saturation transfer, which have widely varied utility in NMR spectroscopy, as reviewed in Freeman (1988). There are several studies that, while not the same as the experiment described here, utilize similar basic concepts. Selective inversion has been used in ^{129}Xe NMR studies to monitor interstage exchange in a zeolite (Larsen et al., 1993; Jameson et al., 1994), to demonstrate that two xenon

populations are coupled (Ripmeester and Ratcliffe, 1993), and to measure diffusion coefficients in polystyrene (Simpson et al., 1995).

In the presaturation experiment we irradiated only a portion of the frequency range covered by the adsorbed xenon signal, using a low power presaturation pulse followed by a high power 90 degree pulse. We are interested in whether and to what extent the irradiation produces saturation of the signal. If saturated, the xenon atoms do not give an NMR signal when the 90 degree pulse is applied. The key ideas used in conceptualizing this experiment are as follows: NMR signals from ^{129}Xe adsorbed in and outside the coal particle are distinguishable; and the possibility that xenon atoms are to some degree mobile means that a xenon atom that is saturated while in one environment can move to another in a given time frame, carrying the saturation with it. (Spin-lattice relaxation is a competitive process.) Possible outcomes of a presaturation experiment are as follows:

(1) The xenon atoms are in distinct internal adsorption sites and are effectively immobile during the time the pulse is applied. In this case we would expect to see a well defined break or a dip in the outline of the adsorbed gas signal in the area where the low power pulse was applied.

(2) The xenon atoms do have distinct internal adsorption sites, but exchange among them during the presaturation time. Here we would expect to see saturation of the adsorbed gas signal, or overall loss of signal intensity, which may be accompanied by a change in the signal shape.

Note that outcomes (1) and (2) are related in that they are only distinguished by the time frame of site to site motion. For example, if the xenon atoms sample all the sites in 100 ms, then in a 10 ms period they are effectively immobile in their adsorption sites. A 10 ms presaturation pulse, assuming it is sufficiently narrow and delivers enough power to cause saturation, would be able to selectively saturate a portion of the overall adsorbed gas signal. A 100 ms pulse, however, should saturate the entire signal. Variation of the time frame of the experiment can identify the transition from one effect of presaturation to another.

(3) Xenon atoms are exchanging both into and out of the particle during the time the sample is presaturated. In this case, we would expect the intensity of both adsorbed and external surface signals to decrease or completely saturate.

(4) The linewidth is not due to a distribution of sites, but to a short T_2 and/or magnetic field inhomogeneity. The signal intensity could be decreased by presaturating the peak maximum, but the shape should remain the same, and presaturating the signal off center should have much less or no effect.

EXPERIMENTAL

Powdered samples of Wyodak subbituminous (subB; 76.3% C) and Sewell medium volatile bituminous (mvb; 88.9% C) coals were obtained from the Penn State/DOE coal sample bank and sieved to 60-100 Tyler mesh particle size. They were dried overnight in 10 mm NMR tubes with rototite valves (Wilmad), heated to 90° C for 2 to 4 hours, then kept under vacuum at room temperature for 24 hours or more. Once dry, the samples were charged with xenon to ~ 1 atm pressure (730-760 torr). Equilibration time was 8-12 hours.

NMR spectra were acquired on a Bruker AMX 360 NMR spectrometer operating at 99.61 MHz. A low power presaturation pulse was applied with the carrier frequency centered on the signal of interest followed by a 90 degree high power pulse and 3 s delay. The low power pulse length was varied as described in the next section. Spectra were run 300 to 1000 scans depending on the individual sample. All sets of spectra for a particular sample were run the same number of scans. Xenon gas at 700 torr was used as an external chemical shift reference.

RESULTS AND DISCUSSION

The ^{129}Xe NMR spectrum of coal and effect of presaturation. The ^{129}Xe NMR spectrum of xenon gas adsorbed on Sewell coal is shown in Figure 1a.

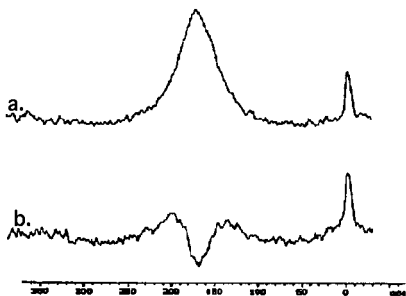


FIGURE 1. ^{129}Xe NMR spectrum of Sewell coal with (a) 80dB presaturation pulse, which has negligible effect and (b) 37 dB presaturation pulse centered at 21870 Hz (approx. 174 ppm).

A presaturation pulse of negligibly low power was applied. The appearance of this spectrum is like that of a ^{129}Xe NMR spectrum of a high rank coal without presaturation. The signal centered at 174 ppm is from xenon adsorbed on the internal surfaces of the coal, and that at 0 ppm is the interparticle or external gas signal. Figure 1b shows the loss of a portion of the signal when a 37 dB presaturation pulse was applied for 0.3 ms at the center of the signal.

Two coals were presaturated on the principal adsorbed xenon signal for increasing lengths of time. The reference spectra for both coal samples are presaturated on the center of the adsorbed gas signal at very low power (80 dB power for 0.1 ms). All subsequent spectra for a given sample were phased relative to the reference.

The Sewell coal was presaturated at 37 dB on the 174 ppm adsorbed xenon signal (21,870 Hz) for increasing times from 0.3 ms to 800 ms. The results are shown in Figure 2. There is a 'hole' in the signal at 0.3 ms accompanied by overall intensity loss. A spectral hole, or the loss of a portion of the adsorbed xenon signal, is evidence that some of the xenon atoms contributing to a broad signal have a resonant frequency close to the applied pulse; some do not, however, hence the residual portions of the signal. This is evidence that the signal is broad due to an overlap of chemical shifts, which in turn indicates that there exist slightly different adsorption sites from which the different xenon chemical shifts arise. At 1 ms the signal is almost saturated. There was no effect on the interparticle gas signal. Upon increasing the pulse length the saturation extends to the remainder of the signal it is focused on, and to the external gas signal. This clearly illustrates the motion of saturated xenon through the solid and out into the interparticle space. At 200 ms, the adsorbed signal in Sewell coal was completely saturated while the interparticle gas signal was less intense. At 400 ms the gas signal intensity decreased noticeably, and at 800 ms it was nearly saturated.

The Wyodak coal was presaturated at 40 dB power at about 150 ppm (20,000 Hz) for increasing times from 1 ms to 40 ms. The results are shown in Figure 3. The spectra show a 'hole' at 1 and 2 ms which is almost saturated at 5 ms. From 1 to 5 ms, the interparticle gas signal at 0 ppm is unchanged. At 10 ms, the adsorbed signal is completely saturated and the interparticle gas signal has some intensity loss. At 30 ms the gas signal is reduced to a little over the noise level, and at 40 ms it is saturated.

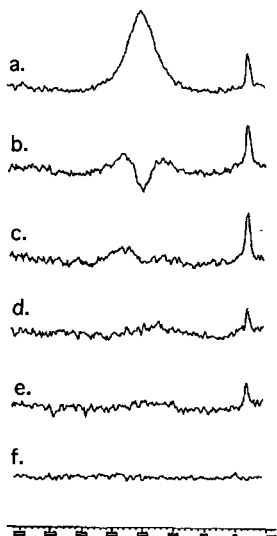


FIGURE 2. Effect of increasing presaturation pulse length on ^{129}Xe NMR spectra of Sewell coal. (a) Reference; (b) 0.3 ms; (c) 1 ms; (d) 200 ms; (e) 400 ms; (f) 800 ms.

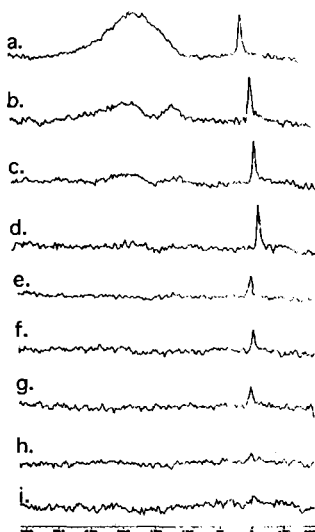


FIGURE 3. Effect of increasing presaturation pulse length on ^{129}Xe NMR spectra of Wyodak coal. (a) Reference; (b) 1 ms; (c) 2 ms; (d) 5 ms; (e) 10 ms; (f) 15 ms; (g) 20 ms; (h) 30 ms; (i) 40 ms.

Implications for the porous structure of the coals. In the Wyodak coal, the adsorbed gas signal survives presaturation longer than the Sewell coal. The longer time for the saturation transfer from the 'hole' effect to saturation of the entire signal is coupled with much shorter time to saturate the external surface signal compared to the Sewell coal. We interpret this as indicating that in the Wyodak coal, it takes a longer time for saturated xenon atoms to exchange among the internal sites and a shorter time for their exchange with gas at the external surface. This indicates that the Wyodak coal has a wider distribution of internal adsorption sites and greater connectivity of the pore network to the outside. The Wyodak coal, at 76.3%C, has meso- as well as microporosity as determined by N₂ and CO₂ adsorption, as is expected based on its rank (Gan et al. 1972). The NMR data in this study is in keeping with the presence of larger pores, in which diffusion of xenon would be faster, acting as feeder pores to the microporosity in this coal.

In the Sewell coal, an apparently shorter time to exchange among the internal sites indicates a narrower distribution of adsorption sites than in the Wyodak coal. It should be noted that the signal itself, without presaturation, is narrower than in the Wyodak coal. This too is an indication of greater site homogeneity. The longer time saturate to the external surface gas signal shows that the access of adsorbed xenon to the external surface in the Sewell coal is far more restricted than in the Wyodak coal. This indicates a significantly different type of pore network in the two coals. The evidence points to a greater number of internal pore network connections than there are openings to the external surface in the Sewell coal. This is consistent with the notion of a highly interconnected microporous system lacking a significant amount of larger porosity.

In both coals the complete saturation of the adsorbed xenon signal, with no portion resistant to saturation after allowing 1-20 ms for xenon to exchange among internal sites with the presaturation pulse applied, demonstrates *interconnection* of porosity. This information could be useful in resolving the continuing controversy on whether coal micropores are primarily open or closed (Larsen et al., 1995; Walker and Mahajan, 1993). There was no isolated adsorbed xenon signal for either coal, an indication that the xenon atoms are moving through an open porous network. If a significant portion of the porosity existed as isolated pockets, movement of xenon through the coal would require passing through regions of both solid matrix and pores. If dissolved in the solid, an NMR signal would be expected either resolved from xenon that is in porosity, or overlapped but detectable as a portion of the signal with a longer lifetime in the saturation transfer experiment. It is very unlikely that xenon can diffuse through the solid matrix at a rate comparable to its passage through pores, and this experiment reveals no indication in either coal that a detectable proportion of the adsorbed xenon is dissolved in solid coal.

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